Phase change behaviour in nitrogen-doped $Ge_1Sb_2Te_4$

M. Osiac[1], V. Tiron[2], G.E. Iacobescu[1]

[1]*University of Craiova, Department of Physics, A.I. Cuza Street, no. 13, Craiova 200585, Romania*
[2]*Alexandru Ioan Cuza University, Faculty of Physics, Blvd. Carol I nr. 11, Iași 700506, Romania*

Nitrogen-doped and undoped $Ge_1Sb_2Te_4$ films were deposited using high-power impulsed magnetron sputtering. The X-ray diffraction patterns showed crystallization to undoped and nitrogen-doped $Ge_1Sb_2Te_4$ films in the temperature range of 160-340^{o}C. For high nitrogen content in the film, the transition temperature from amorphous and face centered cubic states was established by sheet resistance measurements as a function of the annealing temperature.

1. Introduction

Chalcogenide as GeSbTe (GST) became the promising materials studied for next generation non-volatile memories because of its advantages such as high speed, low power consumption, good endurance, high scalability, and fabrication compatibility with complementary metal-oxide semiconductor process.

Among different type of memories, phase change memory (PCM) uses reversible phase change between the crystalline and amorphous states of chalcogenide materials brought about by Joule heating.

In present, many efforts have been made to improve the phase change characteristics and device performances. It was found that doping is an effective means of tuning the alloy's phase change properties. A variety of dopants such as O, Si, Ag, SiO_2 has been utilized to improve the performances of PCM and PcRAM devices.

The nitrogen-doped GST was found also important for improving the performances of PRAM. When nitrogen is doped into a GST film, it exists in the forms of nitride or N_2 molecules, which could suppress crystalline grain growth [1].

Unlike to $Ge_2Sb_2Te_5$ (GST-225), another type of chalcogenide as $Ge_1Sb_2Te_4$ (GST-124) is used in the present work to be doped with nitrogen. However, most studies on the incorporation of nitrogen into GST film have centered on the macroscopic nature of the structural and electrical properties.

In the present work, amorphous GST-124 thin films were synthesized using high-power impulsed magnetron sputtering (HiPIMS). The main advantages of HiPIMS technique is a large increase in the ionization degree of the metallic vapor, where it has been shown that the HiPIMS plasma generates large quantities of highly energetic ions [2] with a directed flux of charged species [3].

2. Experimental

The GST-124 films were deposited by using a magnetron plasma deposition facility with a 3" torus magnetron. The chamber was pumped down to a pressure of 1×10^{-5}Pa before introducing the sputtering gas. Argon and Nitrogen were used as sputtering gas under a total pressure of 0.66 Pa. The films were deposited from a 3"diameter×0.2" thick $Ge_1Sb_2Te_4$ ceramic target (provided by Kurt J. Lesker) onto silicon substrates axially placed in the deposition system. Target to substrate distance was about 8cm and the sputtering was carried out for 15 minutes at 30W.

The target peak power of 10-15 kW was attained during the HiPIMS operation (for – 950 V applied voltage, pulse width of 20 μs and pulse frequency ranged between 100 and 200 Hz). A 1:100 high voltage probe measured the target voltage.

The as-deposited films were isothermal annealed in vacuum at different temperatures between 100-400^{o}C, each sample was annealed for 20 minutes at base pressure of $1.33x10^{-2}$Pa. The thickness of the film are around 300nm.

3. Results and discussions

The XRD analyses established the presence of the amorphous and crystalline phases in the GST-124 coatings. The as-deposited films were growth in amorphous phase in HiPIMS discharge [4].

In this study, nitrogen-doped GST-124 and un-doped GST-124, were deposited on Si substrates.

The nitrogen-doped GST-124 and undoped GST-124 films were annealed in the temperatures range of 100-340°C, to investigate the characteristics of crystallized films. Figures 1-2 show the XRD pattern of the nitrogen-doped and undoped GST-124 films annealed at temperatures 150°C and 200°C, respectively. The annealing time is 20 min in vacuum. In figures 1-2 the XRD pattern is presented for 1.8% and 3.7% nitrogen content in GST-124 film. It can be seen from figures 1-2 that the amorphous state of the nitrogen-doped GST-124 films is preserved in the temperature range 160-200°C.

For the annealing temperature range of 160-200°C, the undoped GST-124 films show a mixing beetwen the amorphous and the metastable states face centered cubic (fcc) with difraction peaks (200) at 29.8 degree and (220) at 42.8 degree, respectively.

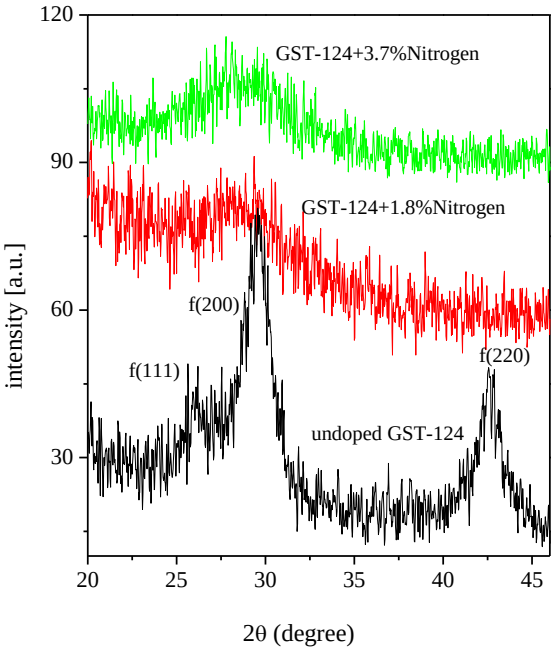

Figure 1.
The XRD patterns for 1.8% and 3.7% nitrogen-doped GST-124 and undoped GST-124 films. The annealing temperature was 160°C.

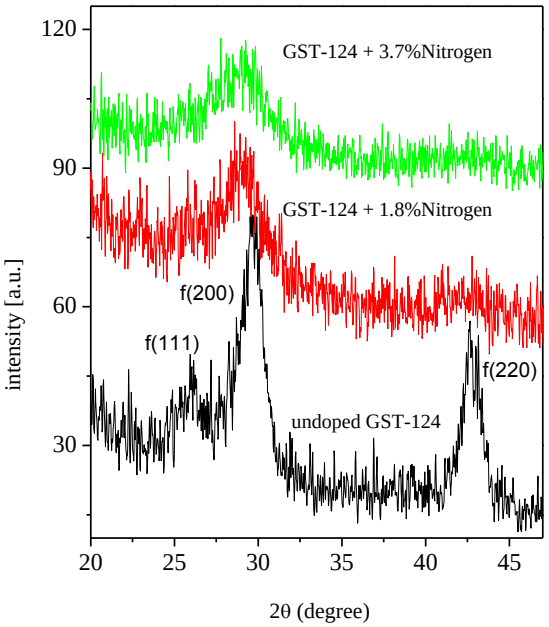

Figure 2.
The XRD patterns for 1.8% and 3.7% nitrogen-doped GST-124 and undoped GST-124 films. The annealing temperature was 200°C.

The diffraction peak (200) to nitrogen-doped GST-124, at annealed temperature of 200°C is visible shifted to lower angle, indicating an increase in the lattice parameter of GST-124.

Figures 3-4 show the XRD pattern of nitrogen-doped and undoped GST-124 films. It can be seen that an increase of the annealing temperature in the range 250-340°C presents for the nitrogen-doped GST-124 film a fcc state with diffraction peaks (200) at 29 degree and (220) at 42 degree, respectively.

The undoped GST-124 film presents a stable hexagonal close packed (hcc) state with diffraction peaks (10-3) at 28.6, (10-6) at 39 degree and (2-10) at 42.9 respectively.

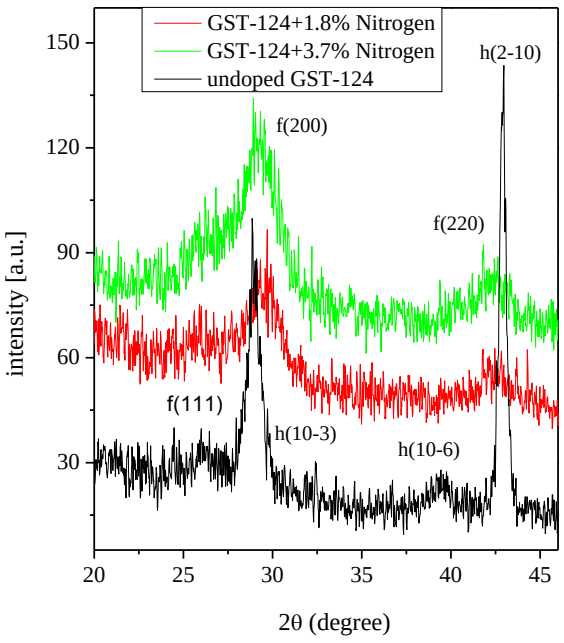

Figure 3.
The XRD patterns for 1.8% and 3.7% nitrogen-doped GST-124 and undoped GST-124 films. The annealing temperature was 250°C.

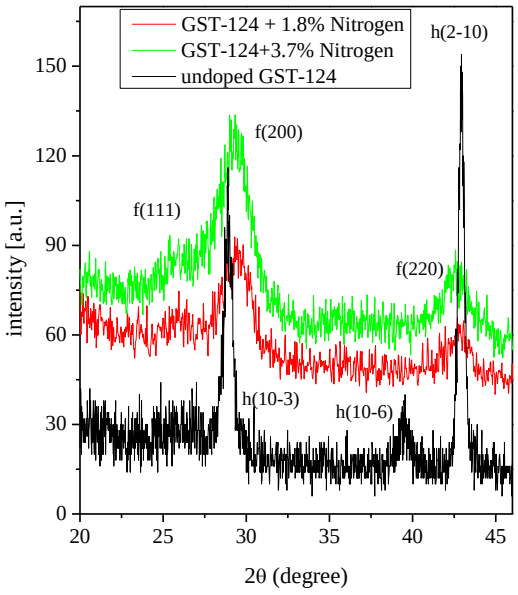

Figure 4
The XRD patterns for 1.8% and 3.7% nitrogen-doped GST-124 and undoped GST-124 films. The annealing temperature was 350°C.

When nitrogen is doped into a GST film, even at smaller content, it could exist in the forms of nitride or N_2 molecules, which suppresses crystalline hcc phase [1].

Sheet resistance as a function of annealing temperature was measured as shown in figure 5.

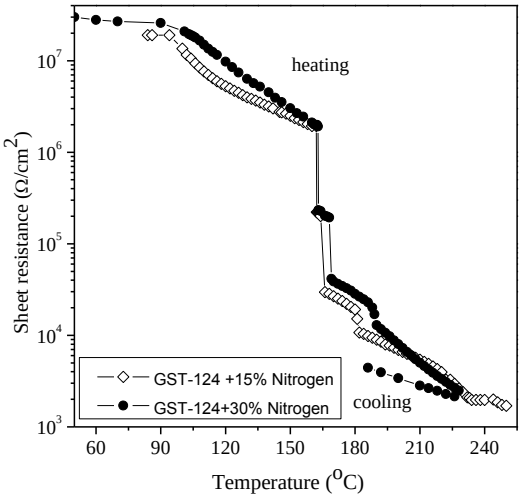

Figure 5.
Plot of sheet resistance as a function of annealing temperature for 15% and 30% nitrogen doped GST-124 film.

Figure 5 shows sheet resistance change in 15% and 30% nitrogen doped GST-124 as a function of annealing temperature. The heating rate in the measurements was fixed at 5 °C/min and the heating of samples was done in vacuum. There were two transition temperatures for nitrogen-doped GST-124 film.

A sharp drop at about 160°C was attributed to amorphous-to-fcc transition. A small drop at about 180°C for 15% nitrogen doped GST-124 and 190°C for 30% nitrogen-doped GST-124, respectively, could be attributed to fcc-to-hcp mixing state.

To understand the nature of transitions at 180°C and 190°C respectively, the XRD measurements where performed after the sheet resistance was measured.

Figure 6 show a mixing of the fcc and hcc phases for 15% nitrogen-doped GST-124, this mixing could be an indication of the second transition.

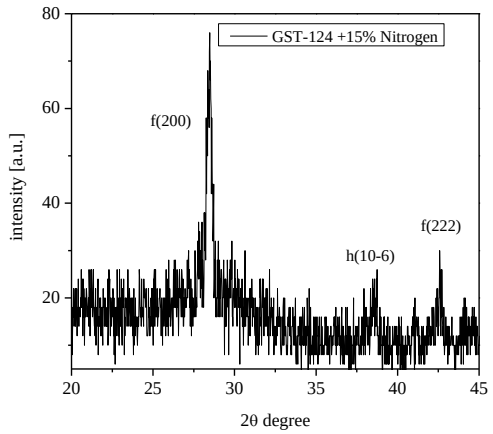

Figure 6.
The XRD patterns for 15% nitrogen-doped GST-124 film presented after sheet resistance measurements. The annealing temperature was 300^{o}C.

For the samples with 15% and 30% nitrogen-doped GST-124, the transition temperature from amorphous-fcc phases was observed at 160^{o}C. Taking into account XRD measurements for 1.8% and 3.7% nitrogen-doped GST-124 films compared with that of undoped GST-124, an increase of the transition temperature from 160^{O}C to 250^{O}C could be observed.

The transition temperature for the undoped GST-124 film is comparable with that of 15% and 30% nitrogen-doped GST-124. An observations of suppressing crystalline fcc phase and decreasing of transition temperature at high amount of gases such as O_2 incorporated in GST-225 films, was also noticed earlier [5].

4. Conclusion

In summary, the crystallization hcc phases were suppressed in the GST-124 film with small amount of nitrogen. The transition temperature has a high change from 160^{o}C for undoped GST-124 film to 250^{o}C for small amount of doped-nitrogen GST-124 film.

Acknowledgments

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5. References

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